DEMINERALIZATION OF CHEDDAR WHEY ULTRAFILTRATE WITH THERMALLY REGENERABLE ION–EXCHANGE RESINS: IMPROVED YIELD OF α–LACTOSE MONOHYDRATE

F. W. PARRISH, P. M. SHARPLES, P. D. HOAGLAND and J. H. WOYCHIK

ABSTRACT

Ultrafiltrate derived from Cheddar cheese whey was demineralized first by removal of divalent cations followed by removal of monovalent cations. The yield of α-lactose monohydrate, crystallized from 50% (W/W) aqueous solution, was significantly greater from the completely deionized solution compared with the yields from ultrafiltrate from which only divalent cations had been removed or from ultrafiltrate which did not receive treatment with thermally regenerable ion-exchange resins.

INTRODUCTION

DURING THE PAST 30 years, a number of applications of ion-exchange resins in dairy technology have been reported. Ion-exchange resins have been used to remove odors and flavors from whey (Meade and Clary, 1949) and nitrogenous compounds from deproteinized whey (Miller and Arrigoni, 1949). Almy and Garrett (1949) employed cation ion-exchange resin treatment of whey to produce a crude product containing 95% lactose, and Hull (1957) removed calcium ions from whey to give improved yield of lactose. Recent developments in demineralization of whey, including the use of ion-exchange resins, have been reviewed (Delaney, 1976).

An analysis of the economic aspects of whey utilization in Europe led Drews (1975) to advocate the production of whey protein concentrate and lactose rather than production of yeast protein, for example. Isolation of whey protein by ultrafiltration has received considerable attention in recent years (McDonough et al., 1971), and the production of crude β-lactose from deionized whey ultrafiltrate has been reported (Kavanagh, 1975).

The availability of thermally regenerable ion-exchange resins and the continuing efforts aimed at improvements in ion-exchange processes (Mansfield, 1976; Anon., 1976) may well result in increased use of these materials and processes in demineralization of carbohydrate-containing solutions.

We report the effect of demineralization of the ultrafiltrate on the yield of lactose by crystallization. For demineralization we used Sirotherm® thermally regenerable ion-exchange resins (Sirotherm is a registered trademark of ICI Australia Limited). These resins, invented by Weiss et al. (1966), are regenerable with hot water instead of with acids and bases, making for reduced operating costs and decreased effluent pollutants (Calmon and Gold, 1976); the major application of these resins to date is in desalination of brackish water (Battaerd et al., 1974).

EXPERIMENTAL

Materials

Cheddar cheese ultrafiltrate (Hargrove et al., 1976) was provided by F.E. McDonough, and was kept frozen until required for use. Sirotherm resins were obtained from Sirotherm Incorporated, Redwood City, CA, and Duolite resins from Diamond Shamrock Corporation, Redwood City, CA. All chemicals used were reagent grade. α-Lactose monohydrate was obtained from Sigma Chemical Co., St. Louis, MO.

Apparatus

Demineralization was performed in 1.6 cm internal diameter, jacketed columns of 100 cm length (Pharmacia, Piscataway, NJ). Water at 25°C or 90°C was circulated through the outer jacket of the columns with a Haake Type F pump (Haake Co., Berlin, West Germany). Ultrafiltrate was passed through the column by a Masterflex pump Model 7013-2 with a Masterflex Model 7020C controller (Cole-Palmer, Chicago, IL). The column effluent was monitored continuously with a Phasar I digital pH meter equipped with a flow-through electrode (Beckman, Fullerton, CA) and with a conductivity meter Model CDM3 equipped with a flow-through cell (Radiometer, Copenhagen, Denmark).

Fractions of the effluent were collected with an Ultrorac Type 7000 fraction collector (LKB, Rockville, MD). Optical rotation of fractions was measured at 589 nm and 20°C with an automatic polarimeter Model 141 (Perkin-Elmer, Norwalk, CT). Atomic absorption analyses were made with a Model 306 instrument (Perkin-Elmer, Norwalk, CT). Sample ashing was performed with an electric furnace Type 056-PT (Hevi Duty Electric Co., Milwaukee, WI). Moisture determinations on lactose crystals were made with a Model KF-3 aquameter (Beckman, Fullerton, CA).

Procedure for demineralization

The following sequence of ion-exchange resin treatments was applied stepwise to the ultrafiltrate, and the various analytical procedures were applied during and after each step in order to assess the effectiveness of treatment: (i) Duolite S-761; (ii) Sirotherm TR-10 ($\bar{X}o = 0.5$); (iii) Duolite C-20 (Na); (iv) Sirotherm TR-10 ($\bar{X}o = 0.1$) in series with Sirotherm TR-20 ($\bar{X}o = 0.1$).

The term $\bar{X}o$ defines the preloading of resin with sodium ions and is related to pH under standardized conditions.

Before use each resin was conditioned by performing five operating cycles of service and regeneration under conditions outlined in the manufacturer's technical bulletins.

Typically, a column of resin (200 ml) was treated with deaerated ultrafiltrate or effluent (1500 ml) from a previous resin treatment at a flow-rate of 60 ml/min (0.3 bed volumes/min) at 27°C, followed by water (300 ml) to remove residual lactose. Fractions (15 ml) were collected. With the Sirotherm resins the temperature of the resin was raised to 90°C while regeneration was performed by downward flow of deaerated softened water (19 ppm total dissolved solids) at 90°C. Four cycles of service and regeneration were performed with each resin.

Regeneration of Duolite S-761 and C-20 was performed with 2M sodium hydroxide and 2M hydrochloric acid, respectively.

Crystallization procedure

The partly or completely deionized ultrafiltrate from each service cycle and ultrafiltrate treated with Duolite S-761 were freeze-dried. Portions, in quadruplicate, were dissolved in deionized water at 65°C to make 50% (W/W) lactose solutions. The solutions were not seeded or stirred and were maintained for 5 min at 65°C then 72 hr at 27°C. The mother liquors were removed from the crystals by centrifugation at 27°C, and the crystals were washed with water at 4°C. The wash water was removed by centrifugation at 4°C, and the crystals were dried at 65°C in vacuum and weighed. Crystallization of α-lactose monohydrate (Sigma) was performed as a control.

Analytical procedures

The purity of the lactose crystals was determined from polarimetric data of initial and final specific optical rotations by use of accurate rotation data provided by Buma and van der Veen (1974).

Moisture determinations were made by the Karl Fischer method for liquid molasses (AOAC, 1975), total nitrogen by a micro-

Authors Parrish, Hoagland and Woychik are with the USDA Eastern Regional Research Center, SEA-FR, Philadelphia, PA 19118. Author Sharples is affiliated with Sirotherm Inc., Redwood City, CA 94064.

Table 1—Cation concentrations of ultrafiltrate during demineralization process

Treatment process step	Cation concentration (milliequivalent/L)			
	Calcium	Magnesium	Sodium	Potassium
None	17.92	5.84	17.66	34.07
Duolite S-761	17.02	5.84	18.44	34.12
Sirotherm TR-10 ($\bar{X}o$ = 0.5)	4.14	0.56	17.18	32.53
Duolite C-20 (Na)	0	0	19.22	32.61
Sirotherm TR-10 ($\bar{X}o$ = 0.1) and Sirotherm TR-20 ($\bar{X}o$ = 0.1)	0	0	0.11	0.02

Kjeldahl method (AOAC, 1975), and ash by an official analytical Method I (AOAC, 1975).

The cations Na, K, Ca and Mg were determined in solutions of the lactose crystals and in ultrafiltrate by atomic absorption analysis with appropriate standards and controls. Conductivity was measured on 3% (W/W) solutions of lactose crystals at 27°C and on column effluents at 27°C and 90°C.

Protein in column effluents was determined by the method of Lowry et al. (1951) with β-lactoglobulin as standard.

RESULTS & DISCUSSION

THE CONCENTRATIONS of calcium, magnesium, sodium, and potassium ions in sweet- and acid-type dry wheys are known to cover wide ranges (Glass and Hedrick, 1977). The ultrafiltrate used in this investigation contained 4.85% lactose, 0.02 mg/g protein N, and 5.7% total solids; the concentrations of major cations (Table 1) are near the upper limit for potassium, near the lower limit for sodium, and close to the mean values for calcium and magnesium, compared with reported values (Glass and Hedrick, 1977). Variations in ionic composition in the ranges reported (Glass and Hedrick, 1977) need be considered only in relation to the capacity requirement for the ion-exchange treatment.

As a preliminary to Sirotherm ion-exchange treatment we chose to treat the Cheddar whey ultrafiltrate with Duolite S-761 to obviate possible irreversible fouling of Sirotherm resins by residual protein in the ultrafiltrate. Duolite S-30, which preceded Duolite S-761, has been used to remove off-color and turbidity from whey products, such treatment being known to be advantageous in the isolation of lactose (Diamond Shamrock Corporation, 1972). In addition, the adsorption and desorption of bovine serum albumin on Duolite S-30 has been reported (Foster et al., 1977). Ultrafiltrate when passed through a column of Duolite S-761 was completely decolorized, presumably by removal of riboflavin; the latter is known to retard crystallization of lactose (Leviton, 1943). Lactose was recovered completely in the effluent based on polarimetric analysis, and 82% of material giving a reaction with Lowry reagent was removed by the resin under the operating conditions. No attempt was made to investigate different operating conditions to improve on the adsorption of this Lowry-positive material. In water treatment with Sirotherm resins the most economic procedure is to remove the divalent cations and monovalent cations in successive steps; this sequence was followed with the effluent from the Duolite S-761 resin. With Sirotherm TR-10 ($\bar{X}o$ = 0.5) 76% of calcium ions, 90% of magnesium ions, and an equivalent quantity of anions were removed while the concentration of sodium and potassium ions was reduced slightly (Table 1). The pH was 6.2 initially and 6.8 finally. The thermally regenerable capacity was 0.15 milliequivalent of divalent cation/ml of resin, and removal of divalent cations in the regeneration step was not less than 93%. An indication of the course of demineralization and thermal regeneration was obtained from the continuous observation of the conductivity of the effluent. The remainder of the calcium and magnesium ions were removed completely with Duolite C-20 (Na), and lactose was crystallized at this stage from a portion of the freeze-dried effluent.

Table 2—Yields of α-lactose monohydrate from treated ultrafiltrate and a control

Source of lactose	Expt. no.	Yield %[a]
α-Lactose monohydrate control (Sigma)	1	67.2 ± 0.6
	2	67.2 ± 0.6
	3	67.3 ± 0.4
	4	67.2 ± 0.3
Deionized ultrafiltrate	1	56.3 ± 1.2
	2	56.3 ± 0.4
	3	56.2 ± 1.1
	4	56.6 ± 0.6
Ca- and Mg-free ultrafiltrate	1	39.4 ± 1.3
	2	39.9 ± 0.3
	3	39.3 ± 0.6
	4	39.6 ± 0.7
Duolite S-761 — treated ultrafiltrate	1	45.0 ± 2.3
	2	42.8 ± 2.3
	3	43.7 ± 0.8
	4	42.6 ± 1.9

[a] Mean of quadruplicate determinations ± standard deviation.

Further treatment with Sirotherm TR-10 ($\bar{X}o$ = 0.1) followed by Sirotherm TR-20 ($\bar{X}o$ = 0.1) was performed to remove sodium and potassium ions. Effluent fractions containing lactose showed a reduction in sodium ion content from 19.22 to 0.11 meq/L, and potassium ion content was lowered from 32.61 to 0.02 meq/L (Table 1). The pH of the effluent was 7.05. Lactose was crystallized from this deionized solution. The presence of lactose did not affect the resin capacity for monovalent cations.

The yields of crystalline lactose from four treatment cycles (Table 2) are the means of quadruplicate determinations. Crystallization was complete in 16 hr for the α-lactose monohydrate control and the completely-deionized ultrafiltrate, but for the calcium- and magnesium-free ultrafiltrate and the Duolite S-761 resin-treated ultrafiltrate about 48 hr were required. Data relating to the purity of the crystalline α-lactose monohydrate products (Table 3) show that the materials crystallized from solutions from which calcium and magnesium ions or all four cations have been removed meet the criteria for edible lactose (Nickerson, 1974). All of these crystals gave clear, colorless solutions at 20% (W/W). The differences in yields (Table 2) for the four types of treatment were all significantly different ($p = 0.01$) from each other when analyzed by means of Duncan's multiple range test. Explanations for these effects of cations on yields of lactose must await more detailed studies of the numerous, complex factors involved in lactose crystallization (Nickerson, 1974), but a primary consideration may be the ability of the common cations found in whey ultrafiltrate to complex with lactose (Nordbo, 1939). The use of the image analyzing computer should have a major impact on fundamental studies of crystal growth of lactose (Valle-Vega and Nickerson, 1977).

Some process alternatives for crystallization of lactose from whey and ultrafiltrate have been discussed (Thurlby and Sitnai, 1976). For convenience and stability considerations under laboratory conditions we chose to freeze-dry the demineralized ultrafiltrate and obtained an amorphous product containing 6.50% moisture and 99.50% lactose on a moisture-free basis. Amorphous lactose, from freeze-drying or spray-drying, is hygroscopic; but nonhygroscopic, high-grade β-lactose (99.0% lactose, 0.2% moisture) has been produced by atmospheric double-drum drying (Bell,

Table 3—Analytical data for lactose crystallized from resin-treated ultrafiltrate and a control source

Analysis	Source of lactose			
	Control (Sigma)	Duolite S-761 — treated ultrafiltrate	Ca- and Mg-free ultrafiltrate	Deionized ultrafiltrate
Lactose %[a]	100.0	98.7	99.6	100.2
Moisture, nonhydrate %	0.12	0.27	0.17	0.12
Protein (N X 6.38) %	0.04	0.06	0.04	0.04
Ash %	0.09	0.65	0.09	0.09
Conductivity (μmhos/cm)[b]	13.4	738	121	6.4
Specific rotation[c]	86.7	85.4	86.2	86.7

[a] As α-lactose monohydrate, based on equilibrium value of $[\alpha]_D^{20} = +52.71°$.
[b] 3% Aqueous solution; water had value of 3.8 μmhos/cm.
[c] Value extrapolated to zero time.

1930). Our demineralized ultrafiltrate should be amenable to double-drum drying to give a high-quality product (cf. Kavanagh, 1975).

Our study shows that thermally regenerable ion-exchange resins can be used to improve the yield of α-lactose monohydrate from whey ultrafiltrate. The salient feature of these resins is that they are regenerated with hot water, obviating the need for acid and base regeneration required for conventional ion-exchange resins. These factors indicate that there may be practical and economic advantages in the use of thermally regenerable ion-exchange resins for isolation of α-lactose monohydrate from whey ultrafiltrate on an industrial scale.

REFERENCES

Almy, E.G. and Garrett, O.F. 1949. Preparation of high-grade crude lactose. U.S. Patent 2,477,558.

Anonymous. 1976. Ion exchange: new design offers continuous processing. Envir. Sci. Technol. 10: 976.

AOAC. 1975. "Official Methods of Analysis," 12th ed. Association of Official Analytical Chemists, Washington, DC.

Battaerd, H.A.J., Cope, A.F.G., Stephens, G.K., Worboys, J.C., Blessing, N.V., Bolto, B.A., Weiss, D.E. and Willis, D. 1974. Desalination of brackish water by thermally regenerable ion exchange. Effluent & Water Treatment J. 14: 245.

Bell, R.W. 1930. Some methods of preparing quickly soluble lactose. Ind. Eng. Chem. 22: 51.

Buma, T.J. and van der Veen, H.K.C. 1974. Accurate specific optical rotations of lactose, and their dependence on temperature. Neth. Milk Dairy J. 28: 175.

Calmon, C. and Gold, H. 1976. New directions in ion exchange. Envir. Sci. Technol. 10: 980.

Delaney, R.A.M. 1976. Demineralization of whey. Australian J. Dairy Technol. 31: 12.

Diamond Shamrock Corporation. 1972. Duolite Data Leaflet No. 4.

Drews, M. 1975. Economics of competing forms of whey utilization. Ber. uber Landwirtschaft 192: 755.

Foster, D.H., Engelbrecht, R.S. and Smoeyink, V.L. 1977. Application of weak base ion-exchange resins for removal of proteins. Envir. Sci. Technol. 11: 55.

Glass, L. and Hedrick, T.I. 1977. Nutritional composition of sweet- and acid-type dry whey. 2. Vitamin, mineral, and calorie contents. J. Dairy Sci. 60: 190.

Hargrove, R.E., McDonough, F.E., LaCroix, D.E. and Alford, J.A. 1976. Production and properties of deproteinized whey powders. J. Dairy Sci. 59: 25.

Hull, M.E. 1957. Ion exchange purification of whey in the preparation of lactose. U.S. Patent 2,778,750.

Kavanagh, J.A. 1975. Production of crude lactose from ultrafiltration permeate. New Zealand J. Dairy Sci. Technol. 10: 132.

Leviton, A. 1943. Adsorption of riboflavin by lactose. Ind. Eng. Chem. 35: 589.

Lowry, O.H., Rosebrough, N.J., Farr, A.L. and Randall, R.J. 1951. Protein measurement with the Folin phenol reagent. J. Biol. Chem. 193: 265.

McDonough, F.E., Mattingly, W.A. and Vestal, J.H. 1971. Protein concentrate from cheese whey by ultrafiltration. J. Dairy Sci. 54: 1406.

Mansfield, G.H. 1976. Salient features in deciding the best design of demineralization plant. Effluent & Water Treatment J. 16: 463.

Meade, R.E. and Clary, P.D. Jr. 1949. Method of making novel products from whey. U.S. Patent 2,465,906.

Miller, O.H. and Arrigoni, L. 1949. Removal of nitrogen from deproteinized whey by ion exchange treatment. Presented at the 116th Meeting of the American Chemical Society, Atlantic City, NJ.

Nickerson, T.A. 1974. Lactose. In "Fundamentals of Dairy Chemistry," 2nd ed., p. 273. Avi Publishing Co., Westport, CT.

Nordbo, R. 1939. The determination of calcium ion activity in biological fluids. Klin. Wochschr. 18: 506.

Thurlby, J.A. and Sitnai, O. 1976. Lactose crystallization: investigation of some process alternatives. J. Food Sci. 41: 43.

Valle-Vega, P. and Nickerson, T.A. 1977. Measurement of lactose crystal growth by image analyzer. J. Food Sci. 42: 1069.

Weiss, D.E., Bolto, B.A., McNeill, R., MacPherson, A.S., Siudak, R., Swinton, E.A. and Willis, D. 1966. An ion-exchange process with thermal regeneration. 2. Properties of weakly basic resins. Aust. J. Chem. 19: 561.

Ms received 7/8/78; revised 9/29/78; accepted 10/5/78.

Presented at the 38th Annual Meeting of the Institute of Food Technologists, Dallas, TX, June 4-7, 1978.

We thank M. Bencivengo (this Laboratory) for nitrogen analyses; D.M. Coleman (Diamond Shamrock Corporation) for providing Duolite resins; F.E. McDonough (Federal Research, Science & Education Administration, U.S. Department of Agriculture, Beltsville, MD) for ultrafiltrate; and J.G. Phillips (Consulting Statistician, Northeast Region, Federal Research, Science & Education Administration, U.S. Department of Agriculture) for statistical analyses.